Manipulating magnetism and conductance of an adatom-molecule junction on metal surfaces: ab initio study

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The state of the art ab initio calculations reveal the effect of a scanning tunnelling microscopy tip on magnetic properties and conductance of a benzene-adatom sandwich on Cu(001). We concentrate on a benzene-Co system interacting with a Cr tip. Our studies give a clear evidence that magnetism and conductance in molecule-adatom junctions can be tailored by the STM tip. Varying the tip-substrate distance the magnetic moment of the Co adatom can be switched on/off. The interplay between spin-polarized electron transport through the junction and its magnetic properties is demonstrated. A spin-filter effect in the junction is predicted.

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The ability to manipulate the magnetic properties and the spin-polarized electronic transport is at the basis of spintronics. In the past few years, much effort has been devoted to engineer and study spin-polarized nanostructures at the atomic level[1, 2, 3, 4, 5, 6, 7, 8, 9]. The development of the scanning tunnelling microscope (STM) has opened the field of local spectroscopy on individual atoms[10]. Spectroscopic measurements performed on magnetic adatoms on metal surfaces have enabled to resolve the Kondo effect arising from the interaction of an adatom with a conduction-electron continuum[11, 12, 13]. The ability to control the spin-state of an isolated magnetic atom has been recently demonstrated[14, 15]. By placing an iron or manganese atom at a specific location on the copper-nitride thin film, Hirjibehedin et al., [14] determined the orientation and strength of the anisotropies of individual magnetic adatoms. Atoms in their experiment can hold a specific magnetic direction, which may allow them to store data. Yayon et al.,[15] have used the direct exchange interaction between a single magnetic atom and a nanoscale magnetic island to fix the spin of the adatom. The above results are of great importance for future atomic-scale technologies and single-atom data storage. Theoretical and experimental studies have shown that electronic and magnetic properties of a single adatom on metal surfaces significantly depend on the tip-surface distance[16, 17, 18].

Recent experiments of Wahl et al.,[19] have demonstrated the ability to tune the spin state of a single magnetic adatom by the controlled attachment of a molecular ligand. The Kondo temperature of a Co adatom on Cu(100) was found to significantly increase with the number of CO molecules attached to the adatom. Zhao et al.,[20, 21] have revealed that the magnetic state of a cobalt ion trapped within a single phthalocyanine molecule (CoPc) on Au(111) can be manipulated by the dehydrogenation of the ligand by voltage pulses from the STM tip. Recent advances in the field of molecular-spintronics have enabled the manipulation of spins in molecules with control down to single spins[22, 23]. Magnetic states of atoms have been found to significantly change in metal-molecule clusters and sandwiches[20, 24, 25, 26, 27, 28]. Controlling and manipulating spins and conductance of single adatoms and molecules on surfaces could be of great importance for the development of quantum nanodevices. Owing to the fascinating advances in single atom/molecule manipulations with a STM tip, it is now possible to engineer new nanostructures in an atom-by-atom fashion[29, 30, 31, 32, 33]. The ability of the STM tip to reversibly modify the internal conformation of a molecule and realize molecular switching has been reported[34].

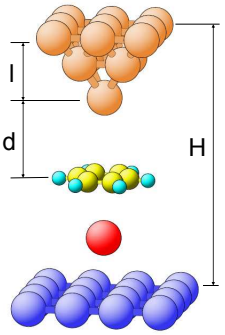

FIG. 1: (color online) Setup for the calculations. H is the distance between the magnetic STM tip and the substrate. l is the length of the tip, while d is the distance between the benzene molecule and the tip-apex.

In this Letter we point out a way for tailoring the spin and the transmission of adatom-molecule junctions

TABLE I: Displacements and magnetic moments of the system for different tip-substrate separations. H is the tip-substrate distance, as shown in Fig. 1. $\Delta l = l - l_0$ is the change of the tip length, where l and l_0 are the tip length with and without tip-benzene interaction. $\Delta d = d - d_0$ is the distance difference between Cr tip-apex and the benzene molecule along z axis after and before full relaxation. The ideal benzene-Co and Co-substrate distances without tip-benzene interaction are 1.60Å and 1.48Å. The last two columns are the magnetic moment of the Cr tip-apex and Co adatom calculated within the GGA(LDA) method.

H (Å)	Δl (Å)	Δd (Å)	M_{Cr} (μ_B)	M_{Co} (μ_B)
>10.1	0	0	4.75(4.68)	0(0)
9.3	0.12	-0.14	4.61(4.61)	0.16(0.08)
8.6	-0.05	0.07	4.24(4.05)	0.64(0.38)
8.1	-0.25	0.28	3.67(3.51)	0.96(0.58)

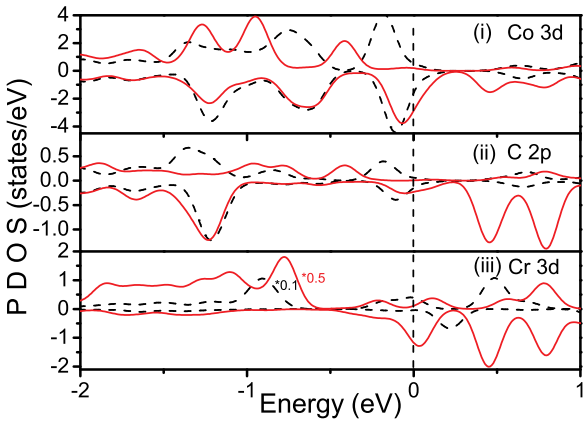

FIG. 2: (Color online) The PDOS of the Co, C and Cr atoms in C_6H_6/Co/Cu(001) junction at two different tip-substrate distances, 9.3Å and 8.1Å. The black lines are the PDOS at a larger tip-substrate distance 9.3Å and the red lines are the PDOS at a closer tip-substrate distance 8.1Å. (i) 3d states of the Co atom, (ii) 2p states of the C atoms in the benzene molecule, (iii) 3d states of the Cr tip-apex. In figure(iii), the values of th PDOS in the region from -2.0 eV to -0.5 eV are scaled by factors 0.5 and 0.1, correspondingly.

on metal surfaces exploiting the tip-molecule interaction. Performing ab initio calculations we show that by means of vertical manipulation it is possible to change the magnetic moment of an adatom and the spin-polarized transmission through the junction. We concentrate on a cobalt adatom sandwiched between Cu(001) and benzene molecule (Fig. 1). We demonstrate that magnetism and spin-dependent transmission in such systems can be controlled by varying the distance between the molecule and the magnetic tip. A spin-filter effect in the junction caused by the tip is revealed.

Our calculations are performed using the density functional theory(DFT) and the linear combination of pseudoatomic orbitals method implemented in the SIESTA code[35]. For the exchange and correlation potential we use both the LDA and the GGA approximation. Atomic cores are replaced by nonlocal, norm-conserving scalar-relativistic Troullier-Martins pseudopotentials. An energy cutoff of 250 Ry is used to define the real-space grid for numerical calculations involving the electron density. Valence electrons are described using a double-ζ plus polarization (DZP) basis set for Cu and the benzene molecule, and a triple-ζ plus polarization (TZP) basis set for the Cr and the Co atoms. The geometries are optimized until all residual forces on each atom are smaller than 0.01eV/Å. The results are confirmed by VASP calculations[36, 37].

In spin-polarized STM experiments, the tip is often made from the nonmagnetic material coated by thin films of antiferromagnetic (AFM) or ferromagnetic (FM) materials [1, 15]. In our study, we model the tip by a pyramid consisting of 13 Cu atoms and one Cr atom for the tip-apex, as shown in Fig. 1 [39].

In order to investigate the interactions between the STM tip and the molecule, we first perform *ab initio* calculations to find an equilibrium position for the benzene molecule adsorbed on the Cu(001) surface. We use a slab model for the adsorption system, consisting of 3, 4 and 5 atomic layers with 16 Cu atoms per layer. Our main results are already well converged for a 3 layers slab. During the geometry optimizations, the structure of the molecule and the top two layers of the substrate are fully relaxed but the bottom layer of the substrate is fixed at its bulk position. Several initial adsorption configurations including hollow, bridge and atop sites are considered to find the most stable one. Comparing the total energies of these configurations, we find that the most stable position of the molecule is over the hollow site of the surface layer, in agreement with the previous experimental [40] and theoretical [41] studies.

We put a Co atom between the benzene molecule and the Cu(001) surface, forming a planar sandwich configurations: C_6H_6/Co/Cu(001)[42]. Such structures are experimentally feasible and can be produced using the STM manipulation[43].

At different tip-substrate distances, the benzene molecule and the Co atom show different relaxation behavior, summarized in Table I. At a larger tip-substrate separation 9.3Å, the benzene molecule, Co adatom and the substrate under the adatom are pulled up, while the Cr tip-apex is pulled down. At this stage the attractive interactions between the tip and benzene molecule, and between the Co atom and the substrate are the driving forces for the observed atomic relaxations. However, at a closer tip-substrate separation 8.1Å, the repulsive interactions between the tip and the benzene molecule, and between the molecule and the Co atom begin to play an important role. It can be observed that the benzene

molecule, Co adatom and the substrate are pushed down, while the tip-apex is pushed up.

The changes of the magnetic moment of the Co adatom during the approach of the STM tip are also summarized in Table I. When the tip-substrate distance is larger than 10.1Å, the tip has very weak interaction with the benzene molecule. Because of the strong hybridization between the C 2p states and the Co 3d states the magnetic moment of the Co in the C_6H_6/Co/Cu(001) system is quenched to $0\mu_B$. When the tip-substrate separation decreases from 9.3Å to 8.1Å, the magnetic moment of the Co atom increases from $0.16\mu_B$ ($0.08\mu_B$, LDA) to $0.96\mu_B$ ($0.58\mu_B$, LDA); on the contrary, the magnetic moment of the Cr tip-apex decreases from $4.61\mu_B$ ($4.61\mu_B$, LDA) to $3.67\mu_B$ ($3.51\mu_B$, LDA).

Partial density of states (PDOS) of the Co atom, C atoms in the benzene molecule and the Cr tip-apex for two different tip-substrate distances, 9.3Å and 8.1Å, are plotted in Fig. 2. At a larger tip-substrate distance (9.3Å), the hybridization between the 3d states of the Cr atom and the 2p states of the C atoms is weak. Meanwhile, the hybridization between the 2p states of the C atoms and the 3d states of the Co atom is still very strong. The minority part of the Co 3d states is slightly shifted to the Fermi level which leads to a nonzero magnetic moment of the Co atom. However, at a closer tip-substrate distance (8.1Å), the 2p states of the C atoms in the molecule are strongly hybridized with the 3d states of the Cr and Co atoms. Also, the hybridization between the C 2p states and Cr 3d states is much stronger than that for the larger distances. The increased interaction between them pushes the minority 3d states of the Cr atom to the Fermi level and increases their population. Therefore, the magnetic moment of the Cr tip-apex reduces from $4.61\mu_B$ to $3.67\mu_B$. However, one should note that due to atomic relaxations in the junction (Table 1) the hybridization between C 2p states and the Co 3d states at a closer tip-substrate distance is weaker than that at a larger distances. Therefore the majority part of the Co 3d states moves far away from the Fermi level (cf. Fig.2). As a result, the magnetic moment of the Co atom at a closer tip-substrate distance recovers from $0.16\mu_B$ to $0.96\mu_B$.

To gain detailed insight into the effect of the tip on the transport properties of the junction, we have performed transport calculations using the TranSiesta [44] code, where the non-equilibrium Green function method is implemented. The results have been calculated with 64 energy points. The bottom of the valence band was at -6 Ry due to the presence of the pseudovalent $3p$ states. Details of transport calculations can be found in [44].

Fig. 3 shows spin-resolved transmission probabilities through the Co-benzene molecule for three different positions of the STM tip. One can see that with decreasing the distance between the tip and the substrate the transmission at zero bias increases. Increasing the distance between the tip leads to quenching of the transmission for the spin-down channel. These results clearly show that such junctions can be used as a well controlled spin-filter.

In conclusion, our findings have demonstrated the ability to tune the spin and the transport properties of a metal-molecule junction by the STM tip. We have shown that the electronic, magnetic and electrical properties of the Co-benzene junction on a Cu(001) surface can be manipulated by changing the tip-substrate distance. Spin-selectivity in transmission can be achieved by an appropriate choice of the position of the STM tip. The physics behind all effects found in this work is related to atomic relaxations in the junction caused by the interaction with the tip. Therefore, we expect that similar effects can be detectable with current technology for different metal-molecule junctions.

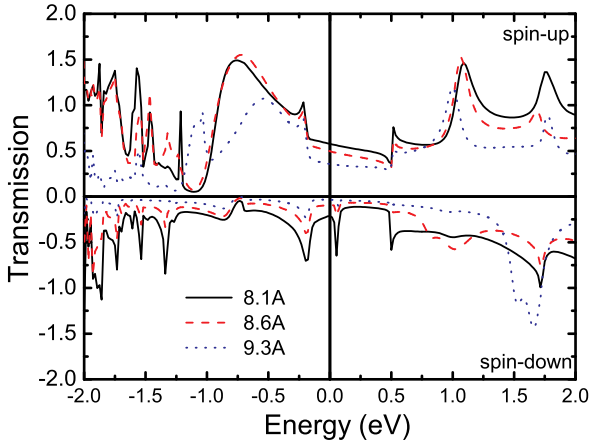

FIG. 3: (color online) The transmission spectra for three different positions of the STM tip. Positive values related for the spin-up channel and negative correspond to the spin-down.

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